

# CH.1 SPECTROCHEMICAL INFORMATION

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# CH.1 SPECTROCHEMICAL INFORMATION

General concepts and basic definitions in the field of spectrochemical analysis

- ✓ Spectrochemical Analysis is one of the major tools of Anal. Chem.

Spectro – chemical → a compound word

Spectrum

Chemical

## Spectrum

a display of the intensity of radiation; emitted, absorbed, scattered by a sample vs. a quantity related to photon energy such as wavelength or frequency.

## Spectrochemical

A spectrum is used to determine chemical species and to investigate the interaction of chemical species with electromagnetic radiation.

## Spectrochemical methods

involve in/direct optical measurement of the photons related to photon energy such as wavelength or frequency.

# 1-1 Radiation/Matter Interactions

- Spectroscopy; the science that deals with the interactions of electromagnetic radiation with matter
- Spectrometry; more restrictive term than spectroscopy and denotes the quantitative measurement of the intensity of electromagnetic radiation at one or more wavelengths with a photoelectric detector.

- There are several types of radiation-matter interactions;  
**1- Ones that involve transitions between specific energy states of chemical species ( absorption, emission)**

EMR is considered composed of discrete packets of energy , photons, and also has a wave character. We can relate the energy of a photon to its wavelength by

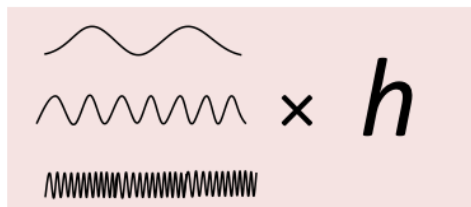
$$\text{Energy of photon } E = h\nu = h \frac{c}{\lambda}$$

The Planck Constant:  $h$

$$h = 6.626 \times 10^{-34} \text{ J s}$$

a proportionality between  
frequency ( $\nu$ ) and energy

$$E = h\nu$$



# 1-1 Radiation/Matter Interactions

2- Ones that do not involve transitions between energy states but rather cause changes in the optical properties of the radiation (e.g. direction and polarization )

- Reflection
- Refraction
- Diffraction
- Scattering

*These interactions are often related to the bulk properties of the sample rather than to specific chemical species. Several analytical techniques are based on these bulk interactions*

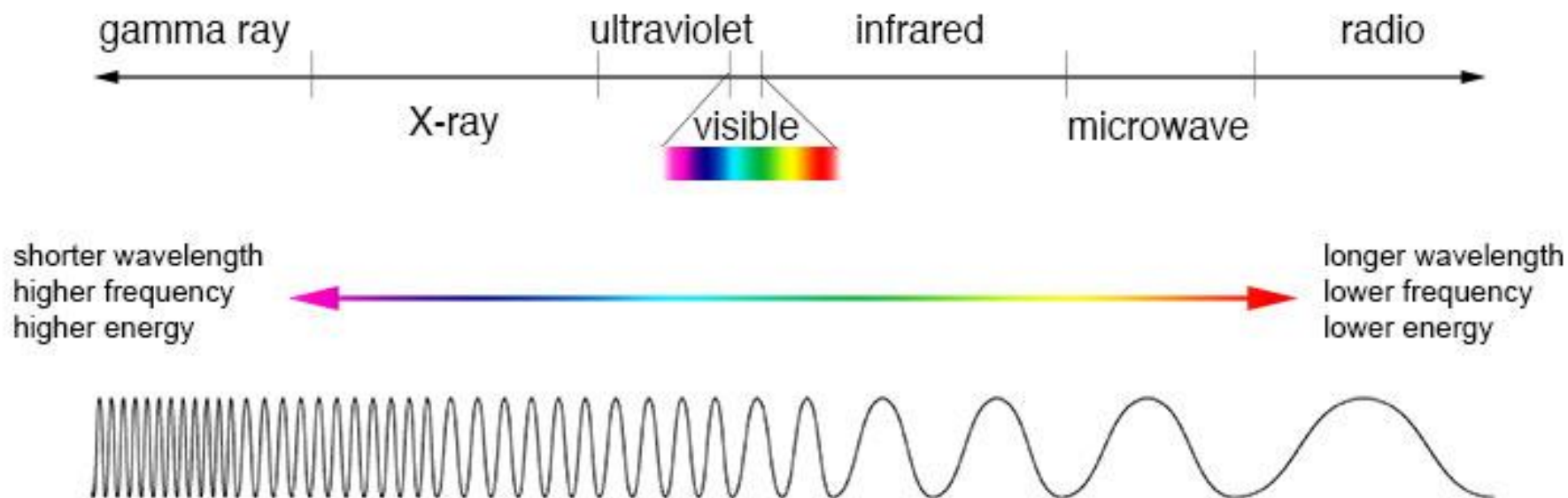
- EMR range for Spectrochemical Analysis; gamma rays ( $> 10^{19}$  Hz) audio freq. ( $< 20$  kHz)
- for Optical Spectrochemical Analysis; UV-Vis-IR (180-50.000 nm)
  - optical requirements are similar
  - the materials used for dispersing, focussing and directing the radiation are conventional optical materials (glass, quartz or alkali halide crystals)
  - Optical Spectrochemical Techniques are divided into ; atomic and molecular spectroscopic techniques.
    - Atomic spectroscopy; free atomic species in the vapor state
    - Molecular spectroscopy; molecular species in the solid, liquid and in vapor st.

# 1-1 Radiation/Matter Interactions

- Photon energies; joules, ergs, electron volts. ( 1 erg=  $10^{-7}$  J) (1 eV=  $1.6 \times 10^{-19}$  J )
- Wavelength of radiation; nm:  $10^{-9}$  m , angstrom:  $10^{-10}$  m, micrometer:  $10^{-6}$  m

$$1 \text{ eV} = 1240 \text{ nm}$$

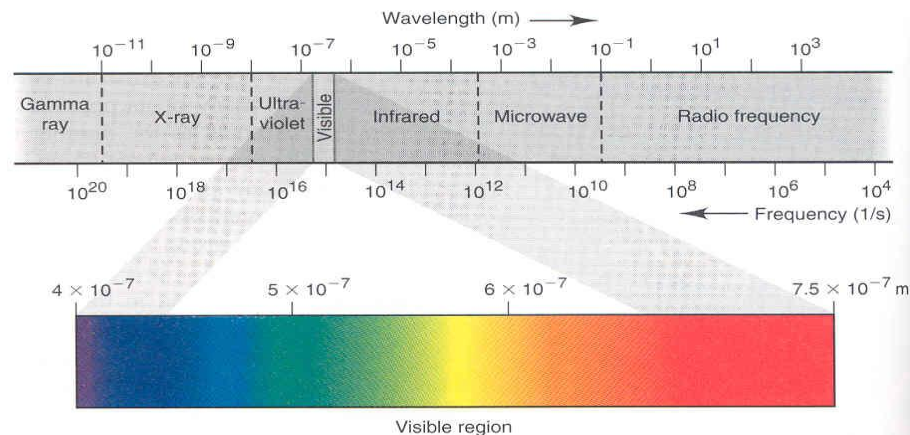
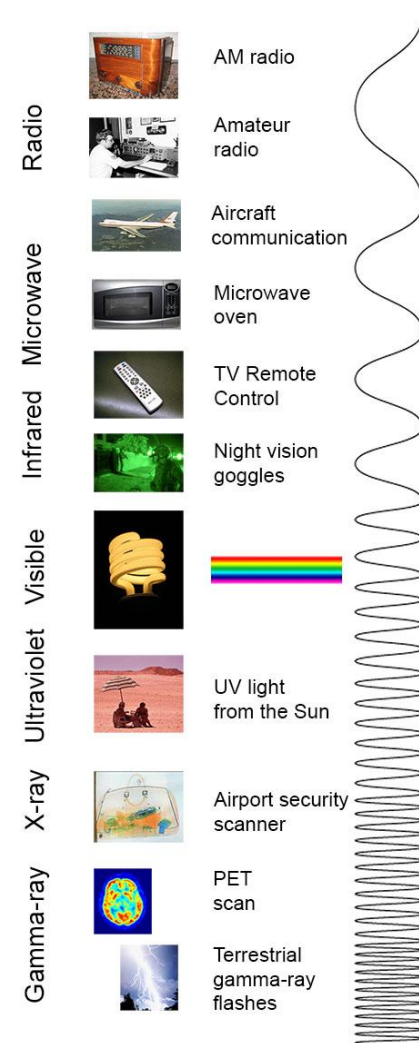
$$\text{Wavenumber} = \bar{\nu} = \frac{1}{\lambda} = \frac{1}{c/\nu} = \frac{\nu}{c} = E/hc$$



# 1-1 Radiation/Matter Interactions

**TABLE 6-1 Common Spectroscopic Methods Based on Electromagnetic Radiation**

Type Spectroscopy	Usual Wavelength Range*	Usual Wavenumber Range, $\text{cm}^{-1}$	Type of Quantum Transition
Gamma-ray emission	0.005–1.4 Å	—	Nuclear
X-Ray absorption, emission, fluorescence, and diffraction	0.1–100 Å	—	Inner electron
Vacuum ultraviolet absorption	10–180 nm	$1 \times 10^6$ to $5 \times 10^4$	Bonding electrons
Ultraviolet visible absorption, emission, and fluorescence	180–780 nm	$5 \times 10^4$ to $1.3 \times 10^4$	Bonding electrons
Infrared absorption and Raman scattering	0.78–300 $\mu\text{m}$	$1.3 \times 10^4$ to $3.3 \times 10^1$	Rotation/vibration of molecules
Microwave absorption	0.75–3.75 mm	13–27	Rotation of molecules
Electron spin resonance	3 cm	0.33	Spin of electrons in a magnetic field
Nuclear magnetic resonance	0.6–10 m	$1.7 \times 10^{-2}$ to $1 \times 10^3$	Spin of nuclei in a magnetic field



# 1-2 Nature of Spectrochemical Analysis

- **Types of Analyses:**
  - **Quantitative analysis**, determination of the amount of particular species
  - **Qualitative analysis**, identification of chemical species.
- ✓ To ascertain the presence of a species with some degree of certainty, we must have at least rudimentary knowledge of the quantity required.
  - ✓ e.g. Hg in river water.
- ✓ **The constituents** determined in a spectrochemical analysis can cover a broad concentration range.
  - ✓ In some cases spectrochemical methods are used to determine **major constituents** in which species present in the range of **1-100 % relative weight range**
  - ✓ **minor constituents** are species present in the range of **0.01-1 % relative weight range**
  - ✓ **trace constituents** are species present in in amounts **> 0.01 % (100 ug/g)**

# 1-2 Nature of Spectrochemical Analysis

- Types of Analyses:
  - ✓ The size of the sample is also used to classify the type of analysis performed
    - ✓ A macro analysis is one carried out on a sample weighing more than 0.1 gram  $> 0.1$  g
    - ✓ A semimicro analysis( mesoanalysis) utilizes a sample size in the range of 0.01 to 0.1 g.
    - ✓ Micro analysis employs a sample size in the range of  $10^{-4}$  -  $10^{-2}$  g
    - ✓ Ultra micro analysis  $< 10^{-4}$  g

*The term ultra trace analysis is considered to be the determination of of a trace constituent in an ultra micro sample*



# 1-2 Nature of Spectrochemical Analysis

- **Samples**

- **Initial sample**; a portion or subset of the bulk material about which analytical information is desired. e.g. : 1 L. of water obtained from a lake to determine Hg content or a few grams of soil from a field to determine conc. of pesticide.
- **Analytical Sample**; a portion of the initial sample presented to the instrument for spectrochemical analysis.
  - In some cases, initial sample is treated : grinding, heating, dissolution, dilution, preconc., separation, etc...
  - The analytical sample should be representative of the sought-for species in the bulk mat.
  - Errors in sample preparation steps are carried through the entire process and lead to errors in final results.

# 1-2 Nature of Spectrochemical Analysis

## Samples:

**Analyte**; the species to be determined in the analytical sample.

**Matrix**; collection of all the constituents in the sample

**Analytical matrix**; matrix of the analytical sample which may differ from the initial sample due to the substances added or removed in sample treatment stages.

**Concomitants**; dictionary meaning, a phenomenon that naturally accompanies or follows something. The matrix as defined here includes the analyte as well as all the other constituents, concomitants.

**Chemical speciation**; determining the concentration of specific chemical forms of the analyte ( e.g.amount of metal in specific oxidation state,  $\text{As}^{+3}$ ,  $\text{As}^{+5}$ , amount of a drug bound to protein etc.)

# 1-2 Nature of Spectrochemical Analysis

## Spectrochemical Phenomena:

Stimulation of species can be brought about by a variety of means including

- (1) bombardment with electrons or other elementary particles, which generally leads to the emission of X-radiation
- (2) exposure to an electric current, an ac spark or an intense heat source (flame, dc arc, or furnace), producing ultraviolet, visible, or infrared radiation;
- (3) irradiation with a beam of electromagnetic radiation, which produces fluorescence radiation; and
- (4) an exothermic chemical reaction that produces chemiluminescence.

**Ground state:** the lowest energy state of the analyte,

**Excited state:** a higher energy state in which the analyte momentarily present due to applied energy.

Spectrochemical information is provided by measuring the electromagnetic radiation **emitted** by the species as it returns to the **ground state** from an **excited level** or by measuring the amount of emr **absorbed** in the excitation process

**Absorption:** Reduction in intensity of EMR

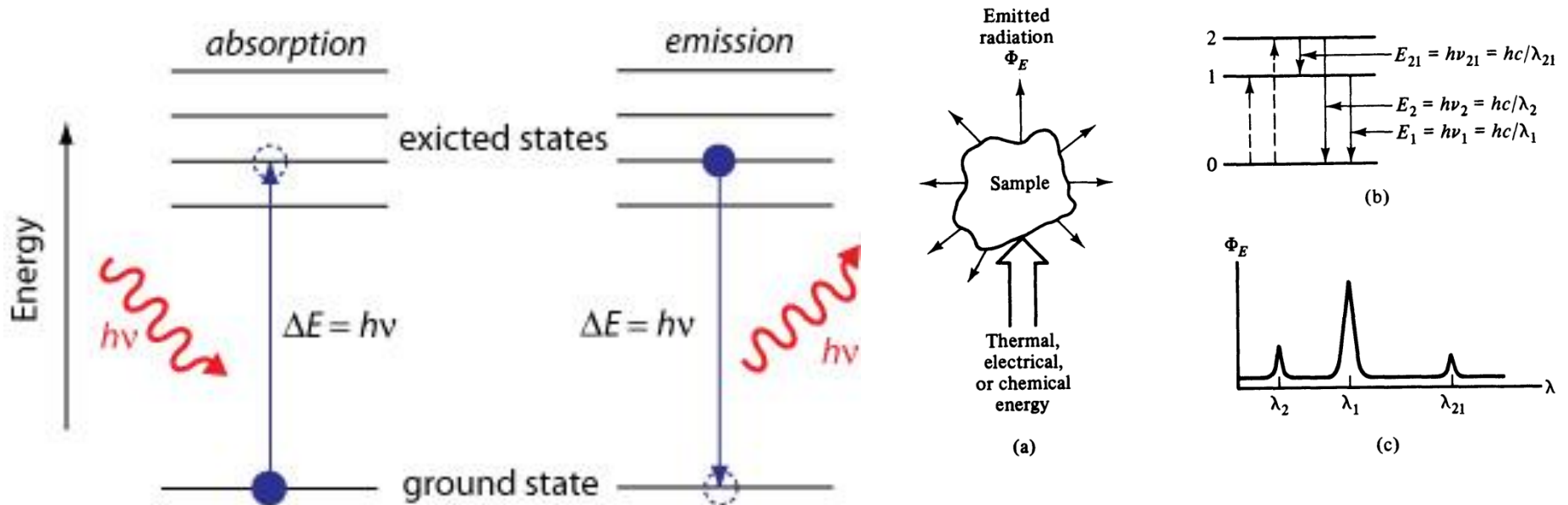
**Emission:** A process of photon being emitted

# Absorption and emission spectroscopy

In *absorption spectroscopy*, we measure the amount of light absorbed as a function of wavelength. This can give both qualitative and quantitative information about the sample.

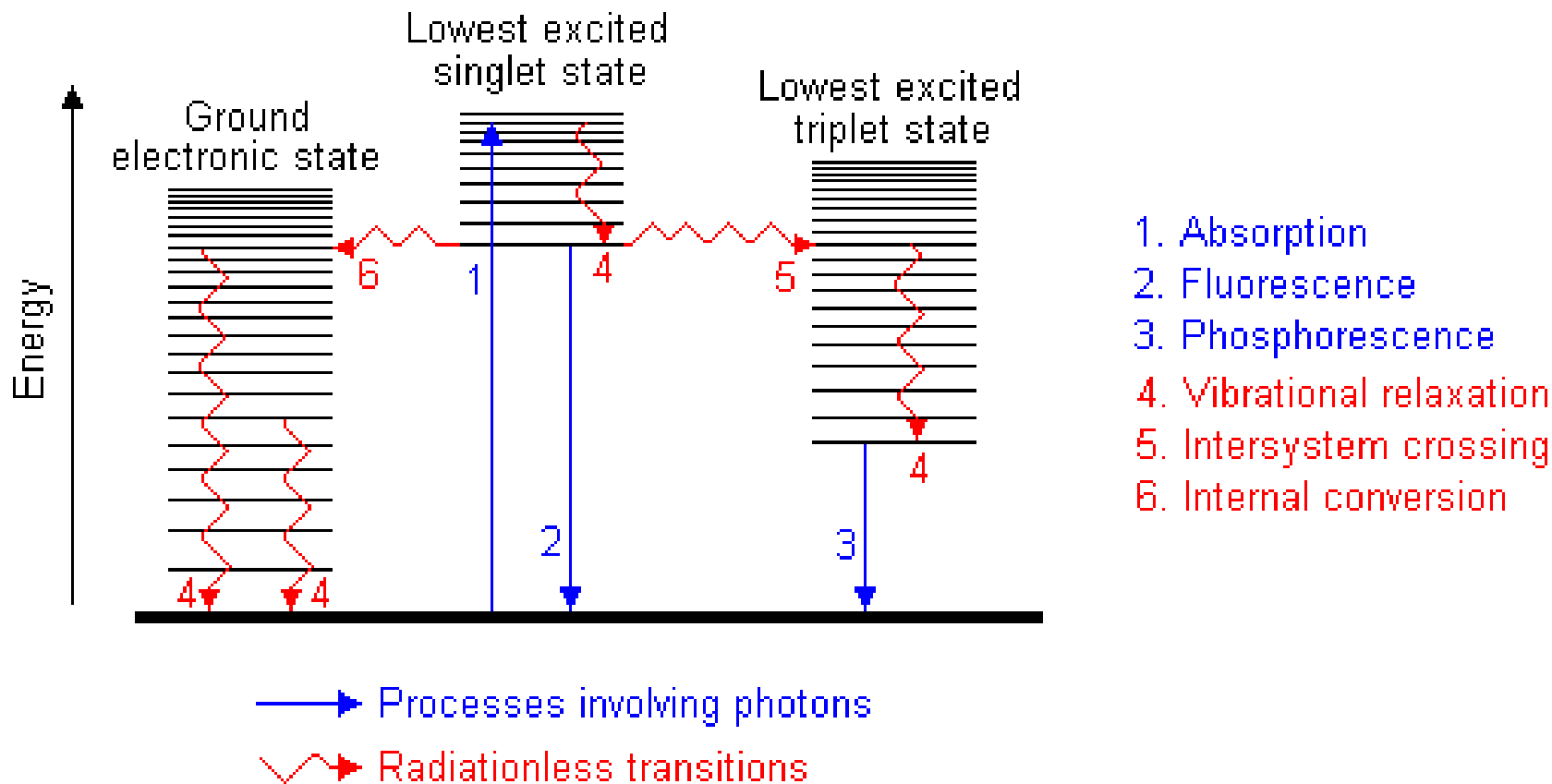
In *photoluminescence spectroscopy* the emission of photons is measured after absorption.

The most important forms of photoluminescence for analytical purposes are *fluorescence* and *phosphorescence spectroscopy*.



# 1-2 Nature of Spectrochemical Analysis

- **Photoluminescence: Fluorescence and phosphorescence**

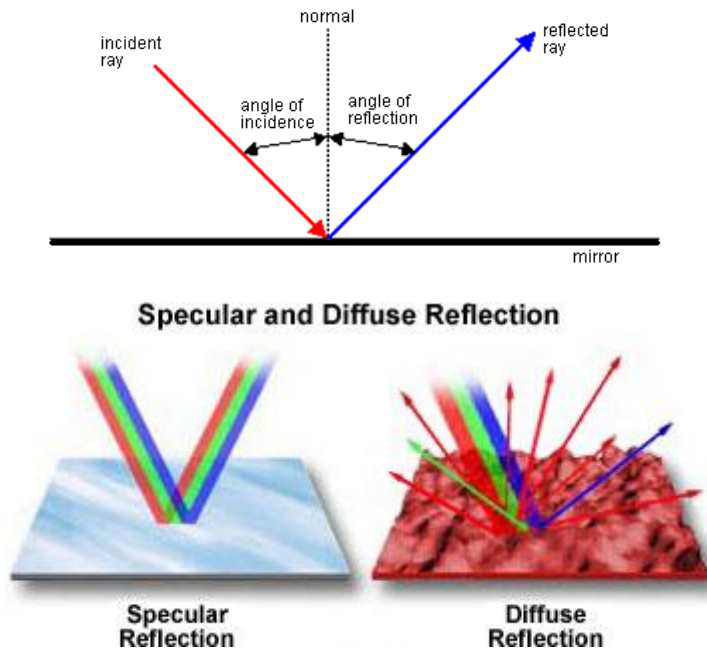


**Chemiluminescence** occurs when a chemical reaction produces an electronically excited species which emits a photon in order to reach the ground state.

# 1-2 Nature of Spectrochemical Analysis

When the sample is stimulated by application of an external EMR source, several processes other than absorption are possible. For example, the radiation can be **reflected, refracted or scattered**.

**Reflection** occurs when light bounces off objects. How much reflection depends upon how even the surface is. If the surface is rough, the light **scatters**. If the surface is smooth and flat, the light will bounce off it at equal angles.



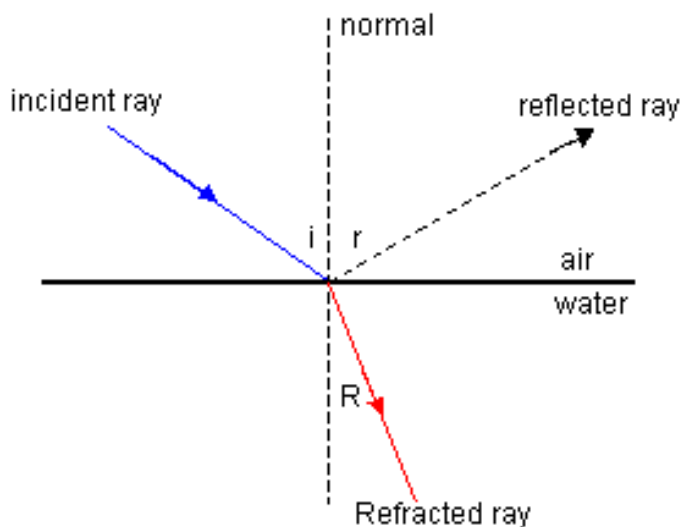
Reflection off of smooth surfaces such as mirrors or a calm body of water leads to a type of reflection known as **specular reflection**. Reflection off of rough surfaces such as clothing, paper, and the asphalt roadway leads to a type of reflection known as **diffuse reflection**. Whether the surface is microscopically rough or smooth has a tremendous impact upon the subsequent reflection of a beam of light. The diagram below depicts two beams of light incident upon a rough and a smooth surface.

## Laws of Reflection

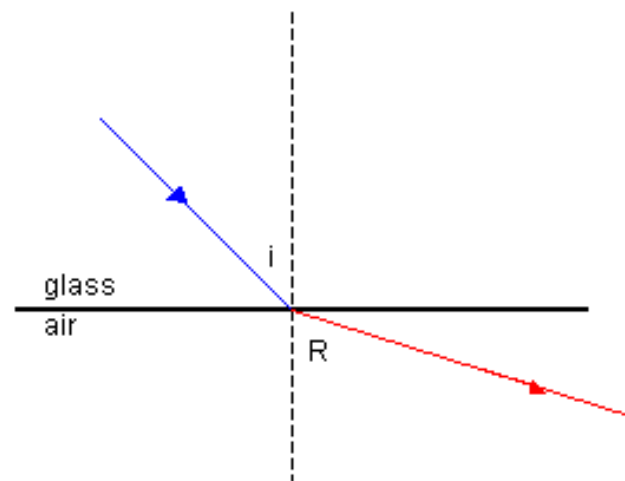
- ✓ The angle of incidence is equal to the angle of reflection.
- ✓ The incident ray, reflected ray, and normal all line in the same plane.

# 1-2 Nature of Spectrochemical Analysis

- **Refraction** is the change in direction of propagation of a wave when the wave passes from one medium into another, that have different densities, an abrupt change in direction, or *refraction*, of the beam is observed and changes its speed.
- Light waves are **refracted** when crossing the boundary from one transparent medium into another because the speed of light is **different** in **different** media.
- When the beam passes from a **less dense to a more dense** environment, the bending is **toward the normal** to the interface. Bending **away from the normal** occurs when the beam passes from a **more dense to a less dense** medium.



$i$  - angle of incidence  
 $r$  - angle of partial reflection  
 $R$  - angle of refraction

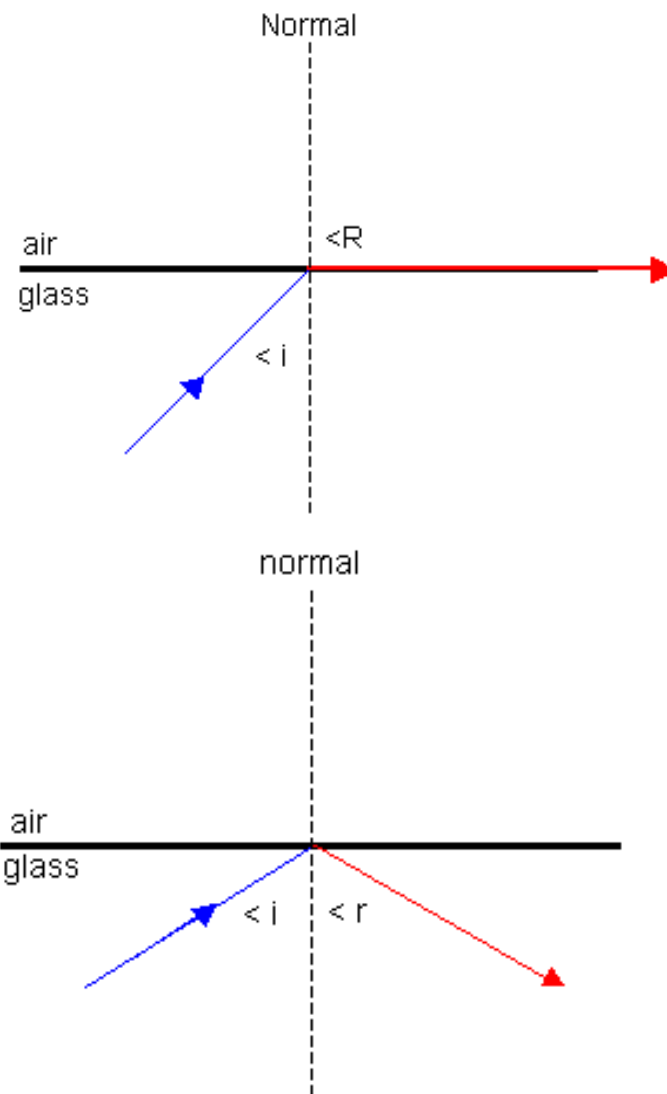


# 1-2 Nature of Spectrochemical Analysis

➤ When light travels from a denser medium to a less dense medium at a very special incident angle, the resulting refracted angle is  $90^\circ$ . This special angle of incidence is called the **critical angle** of that medium.

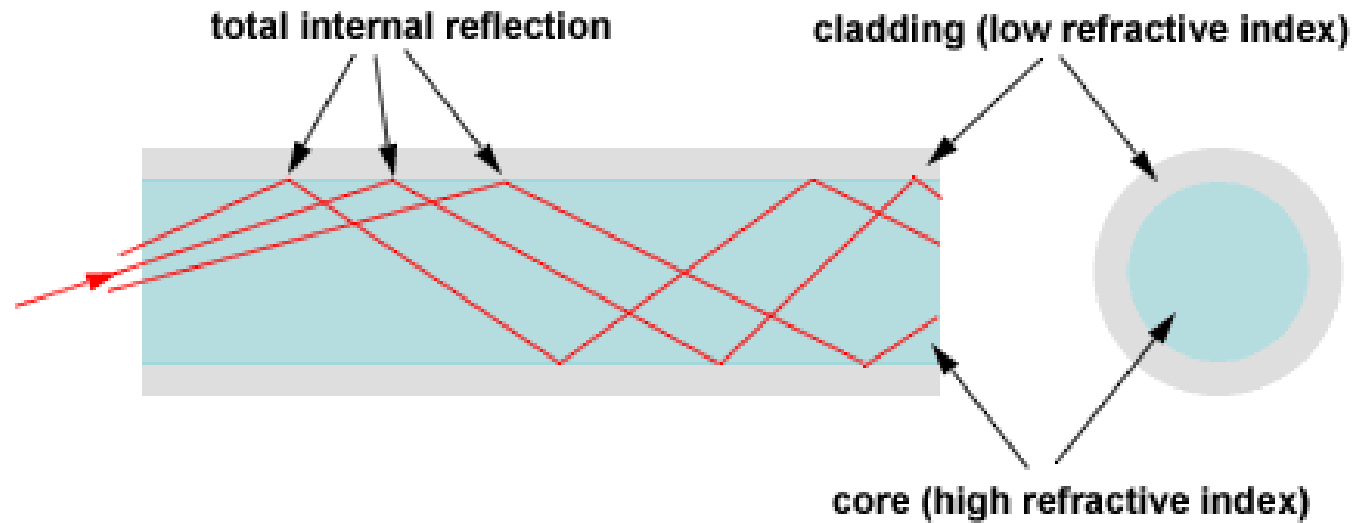
Substances that have a high index of refraction ( $n$ ) have a low critical angle. Diamond has an index of refraction of 2.42 with a critical angle of  $24.5^\circ$ , while water has an index of refraction of 1.33 and a critical angle of  $49^\circ$ .

➤ When light passes into a less dense medium with the angle of incidence **greater than the critical angle**, the light simply cannot exit the medium and is effectively “trapped” in the denser medium and reflects off the surface. It does not pass through and refract. We call this **total internal reflection**.





Optical fibers are based entirely on the principle of total internal reflection



# Optical Fiber's Numerical Aperture (NA)

- Multimode optical fiber will only propagate light that enters the fiber within a certain cone, known as the acceptance cone of the fiber. The half-angle of this cone is called the acceptance angle,  $\theta_{max}$ . For multimode fiber, the acceptance angle is determined only by the indices of refraction:

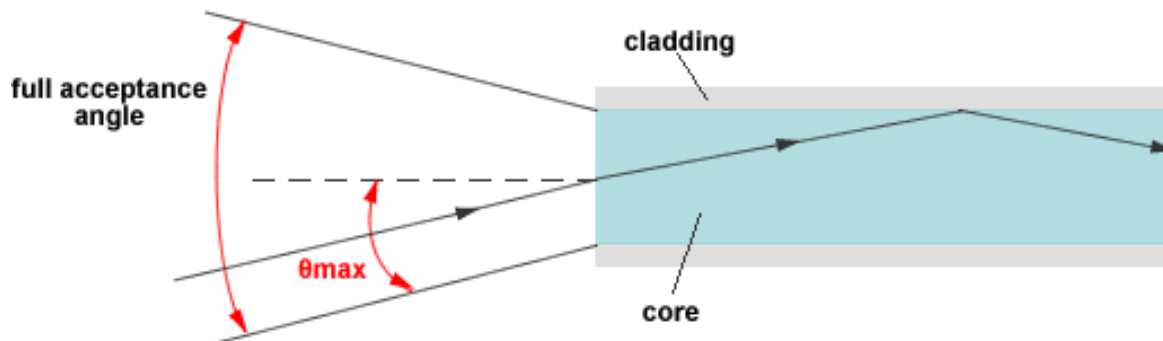
$$NA = n \sin \theta_{max} = \sqrt{n_f^2 - n_c^2}$$

Where

$n$  is the refractive index of the medium light is traveling before entering the fiber

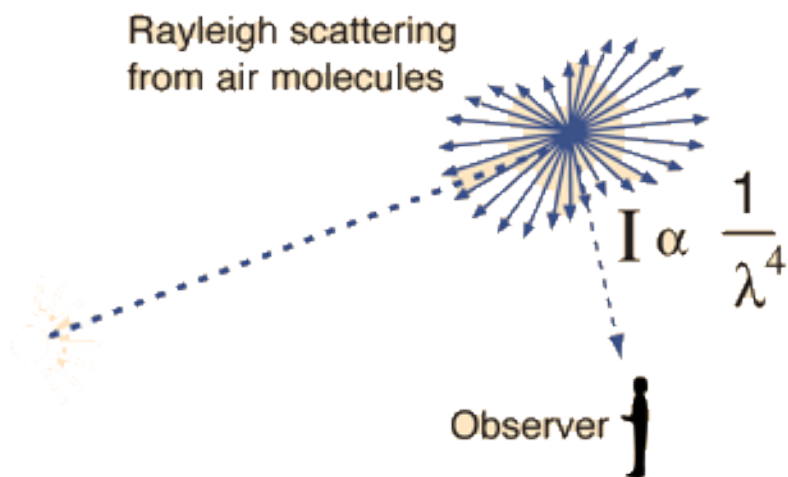
$n_f$  is the refractive index of the fiber core

$n_c$  is the refractive index of the cladding



# 1-2 Nature of Spectrochemical Analysis

- When radiation is scattered, the interaction of the incoming radiation with the sample may be ♣ elastic or ♣ inelastic.
- In elastic scattering, the wavelength of the scattered radiation is the same as that of the source rad. The intensity of the elastically scattered radiation is used to make measurements in *nephelometry and turbidimetry* and *particle sizing*.
- Scattering by *molecules or aggregates of molecules with dimensions significantly smaller* than the wavelength of the radiation is called *Rayleigh scattering*;
  - its intensity is proportional to the inverse fourth power of the wavelength, **the dimensions of the scattering particles, and the square of the polarizability** of the particles.
  - An everyday manifestation of Rayleigh scattering is the blue color of the sky, which results from greater scattering of the shorter wavelengths of the visible spectrum.

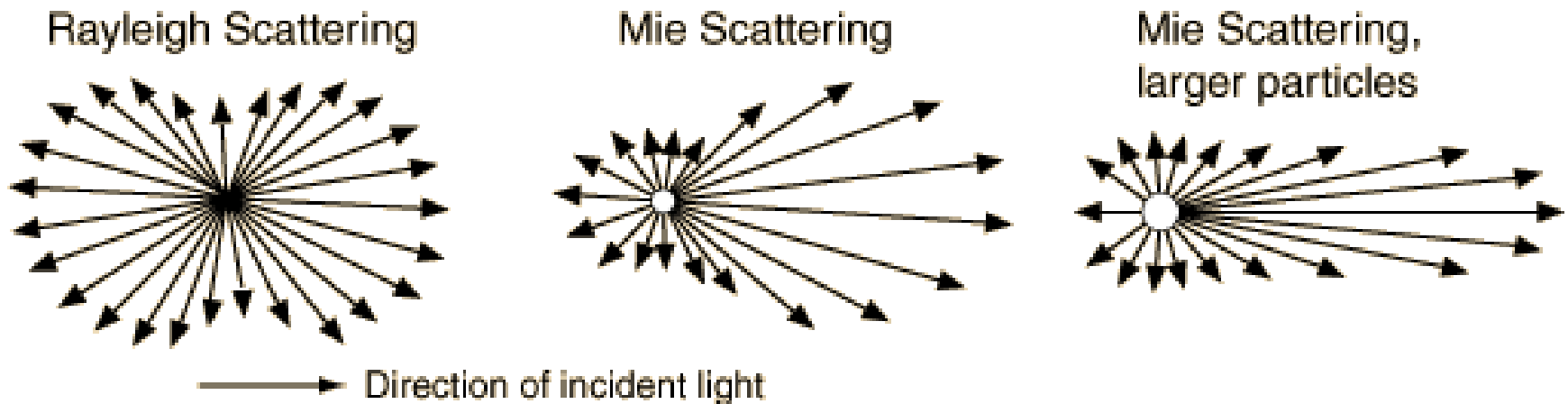


The strong wavelength dependence of Rayleigh scattering enhances the short wavelengths, giving us the blue sky.

The scattering at 400 nm is 9.4 times as great as that at 700 nm for equal incident intensity.

## Mie Scattering

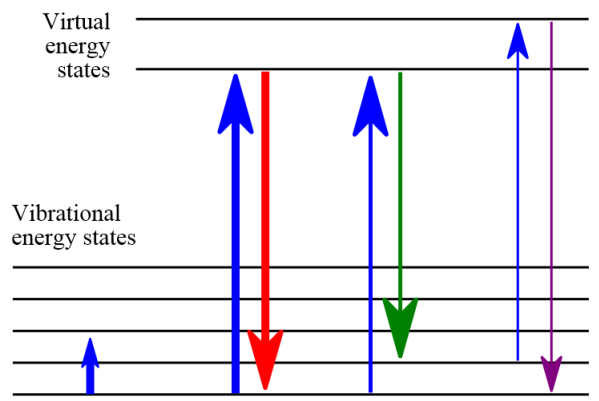
- With large particles, scattering can be different in different directions (Mie scattering). Measurements of this type of scattered radiation are used to determine the size and shape of large molecules and colloidal particles.
- Mie scattering is not strongly wavelength dependent and produces the almost white glare around the sun when a lot of particulate material is present in the air. It also gives us the white light from mist and fog.
- This scattering produces a pattern like an antenna lobe, with a sharper and more intense forward lobe for larger particles.



# 1-2 Nature of Spectrochemical Analysis

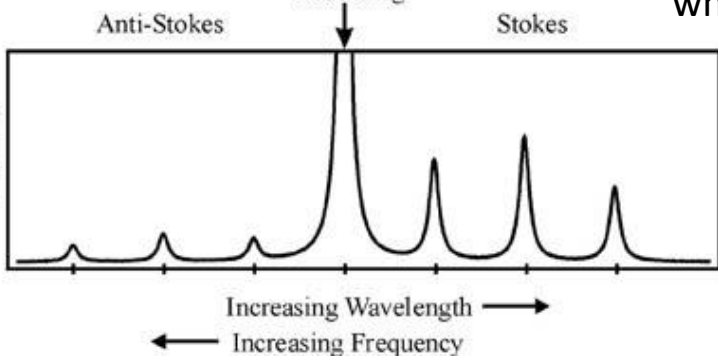
➤ **Inelastic scattering**, the wavelength of the scattered radiation is different than that of the source radiation. Scattering in which the scattered photons have either a higher or lower photon energy is called [Raman scattering](#).

➤ *Raman spectroscopy*, uses inelastic scattering to produce a vibrational spectrum of sample molecules. In this type of spectroscopic analysis, the intensity of the scattered radiation is recorded as a function of the frequency shift of the incident radiation. The intensity of Raman peaks is related to the concentration of the analyte.



✓ If the molecule is in its ground state upon interaction with the probe beam, the light can be absorbed and then re-emitted at a lower frequency, since energy from the light is channeled into the vibrational mode of the molecule. This is referred to as Stokes-shifted Raman scattering.

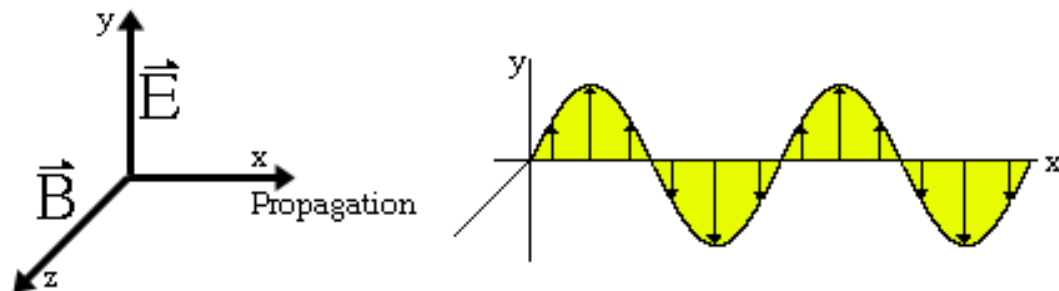
✓ If the molecule is in a vibrationally excited state when it interacts with the probe beam, the interaction can cause the molecule to give up its vibrational energy to the probe beam and drop to the ground state. In this case, the scattered light is higher in frequency than the probe beam). This is referred to as anti-Stokes Raman scattering, which is much less common than Stokes scattering.



➤ The most common occurrence is that light is absorbed and re-emitted at the same frequency. This is known as Rayleigh, or elastic scattering.

# 1-2 Nature of Spectrochemical Analysis

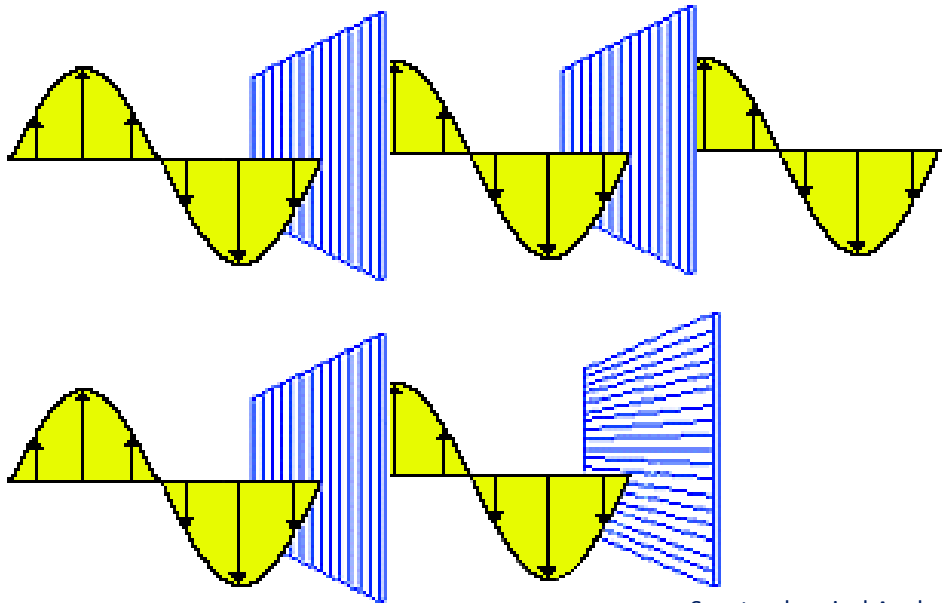
## Light and Polarization



- Light can be represented as a transverse electromagnetic wave made up of mutually perpendicular, fluctuating electric and magnetic fields. The left side of the following diagram shows the electric field in the  $xy$  plane, the magnetic field in the  $xz$  plane and the propagation of the wave in the  $x$  direction.
- Light is considered to be "linearly polarized" when it contains waves that only fluctuate in one specific plane.
- A light wave that is vibrating in more than one plane is referred to as **unpolarized light**. Light emitted by the sun, by a lamp in the classroom, or by a candle flame is unpolarized light. Such light waves are created by electric charges that vibrate in a variety of directions, thus creating an electromagnetic wave that vibrates in a variety of directions. This concept of unpolarized light is rather difficult to visualize. In general, it is helpful to picture unpolarized light as a wave that has an average of half its vibrations in a horizontal plane and half of its vibrations in a vertical plane.

# 1-2 Nature of Spectrochemical Analysis

- A *polarizer* is a material that allows only light with a specific angle of vibration to pass through.
- If two polarizers are set up in series so that their optical axes are parallel, light passes through both. However, if the axes are set up 90 degrees apart (crossed), the polarized light from the first is extinguished by the second. As the angle rotates from **0** to 90 degrees, the amount of light that is transmitted decreases. This effect is demonstrated in the following diagram. The polarizers are parallel at the top and crossed at the bottom

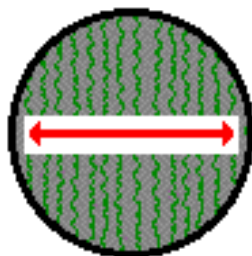


# 1-2 Nature of Spectrochemical Analysis

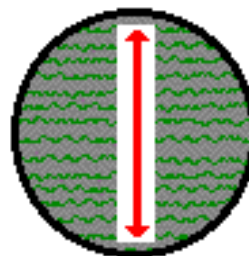
## Polarization by Use of a Polaroid Filter

- A Polaroid filter is able to polarize light because of the chemical composition of the filter material. The filter can be thought of as having long-chain molecules that are aligned within the filter in the same direction. During the fabrication of the filter, the long-chain molecules are stretched across the filter so that each molecule is (as much as possible) aligned in say the vertical direction. As unpolarized light strikes the filter, the portion of the waves vibrating in the vertical direction are absorbed by the filter. The general rule is that the electromagnetic vibrations that are in a direction parallel to the alignment of the molecules are absorbed.

### Relationship Between Long-Chain Molecule Orientation and the Orientation of the Polarization Axis



**When molecules in the filter are aligned vertically, the polarization axis is horizontal.**



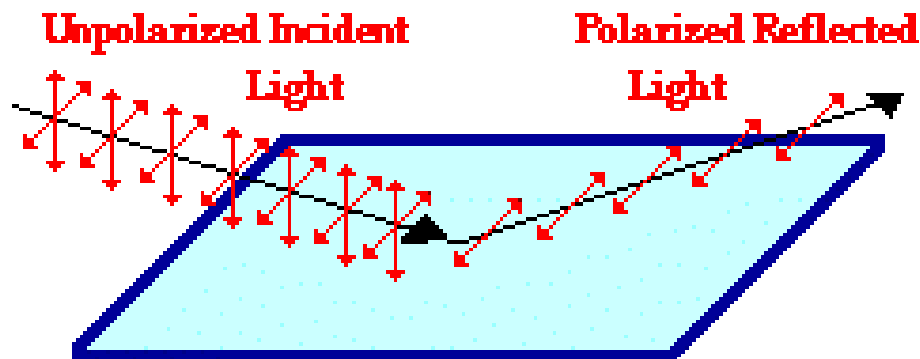
**When molecules in the filter are aligned horizontally, the polarization axis is vertical.**



# 1-2 Nature of Spectrochemical Analysis

## Polarization by reflection

- Unpolarized light can also undergo polarization by reflection off of nonmetallic surfaces. The extent to which polarization occurs is dependent upon the angle at which the light approaches the surface and upon the material that the surface is made of.

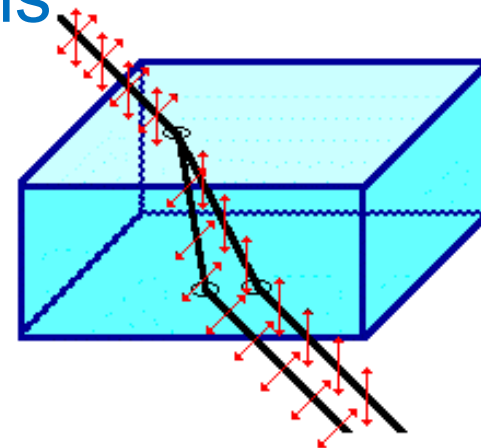


**Reflection of light off of non-metallic surfaces results in some degree of polarization parallel to the surface.**

# 1-2 Nature of Spectrochemical Analysis

## Polarization by Refraction

- Polarization can also occur by the refraction of light. Refraction occurs when a beam of light passes from one material into another material. At the surface of the two materials, the path of the beam changes its direction. The refracted beam acquires some degree of polarization. Most often, the polarization occurs in a plane perpendicular to the surface. The light is *split* into two beams upon entering the crystal.



The two refracted rays passing through the Iceland Spar crystal are polarized with perpendicular orientations.

- Subsequently, if an object is viewed by looking through an Iceland Spar crystal, two images will be seen. The two images are the result of the double refraction of light. Both refracted light beams are polarized - one in a direction parallel to the surface and the other in a direction perpendicular to the surface. Since these two refracted rays are polarized with a perpendicular orientation, a polarizing filter can be used to completely block one of the images. If the polarization axis of the filter is aligned perpendicular to the plane of polarized light, the light is completely blocked by the filter; meanwhile the second image is as bright as can be. And if the filter is then turned 90-degrees in either direction, the second image reappears and the first image disappears. Now that's pretty neat observation that could never be observed if light did not exhibit any wavelike behavior.



Effect of a polarizer on reflection from mud flats. In the picture on the left, the polarizer is rotated to transmit the reflections as well as possible; by rotating the polarizer by  $90^\circ$  (picture on the right) almost all [specularly reflected](#) sunlight is blocked.



The effects of a [polarizing filter](#) on the sky in a photograph. The picture on the right uses the filter.

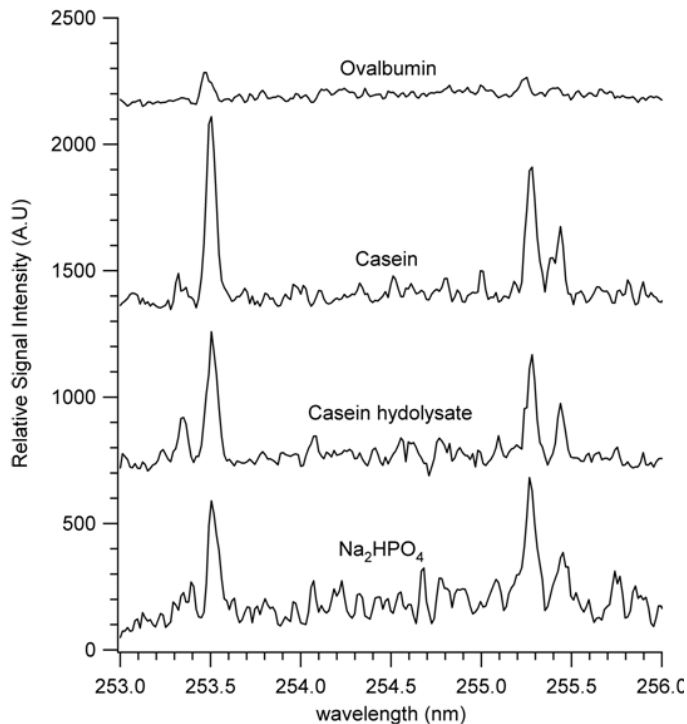
# 1-2 Nature of Spectrochemical Analysis

## Applications of Polarization

- In industry, Polaroid filters are used to perform stress analysis tests on transparent plastics. As light passes through a plastic, each color of visible light is polarized with its own orientation.
- Polarization is also used in the entertainment industry to produce and show 3-D movies. Three-dimensional movies are actually two movies being shown at the same time through two projectors. The two movies are filmed from two slightly different camera locations. Each individual movie is then projected from different sides of the audience onto a metal screen. The movies are projected through a polarizing filter. The polarizing filter used for the projector on the left may have its polarization axis aligned horizontally while the polarizing filter used for the projector on the right would have its polarization axis aligned vertically. Consequently, there are two slightly different movies being projected onto a screen. Each movie is cast by light that is polarized with an orientation perpendicular to the other movie. The audience then wears glasses that have two Polaroid filters. Each filter has a different polarization axis - one is horizontal and the other is vertical. The result of this arrangement of projectors and filters is that the left eye sees the movie that is projected from the right projector while the right eye sees the movie that is projected from the left projector. This gives the viewer a perception of depth.

# Analysis of Real Samples

- In qualitative analysis, the wavelengths of optical transitions are used to identify the presence of a chemical species.
- Quantitative determinations are based on the intensity of the EMR at a given wavelength and its relationship to the analyte concentration.



SAMPLES ARE ANALYZED BUT THAT CONCENTRATIONS OF THE SPECIES ARE DETERMINED

- Analysis of paint for lead or Determination of lead in paint.

# Analysis of Real Samples

- **Blank measurements** are required in nearly all spectrochemical techniques.
- Ideal blank contains all the sample constituents except the analyte.
- The blank is treated as identically as possible with the sample.
- The instrumental response from the blank is subtracted from that of the sample in order to compensate the effect of concomitants.
- An ideal blank can eliminate some type of interference effects due to concomitants but can not compensate for concomitant species that affect the production and measurement of the analyte response.
- It is difficult to prepare an ideal blank, because the concomitants and their concentrations are not usually known.
- **Sample container**, may give rise to additional interference effects due to the optical interactions of EMR with the container walls.
  - in molecular spectroscopy, Glass, quartz, salt cells,
  - in atomic spectroscopy; flame, a plasma, heated chamber., etc. The hot gases produced can emit or absorb radiation which can be a potential source of interference.

## 1.3 Expression of Analytical Information

- How to express spectrochemical information in a convenient manner so that;
  - analyte concentration data can readily be extracted or
  - the dependence of the results on chemical, physical or instrumental variables can easily be summarized.

### Calibration data:

– **Concentration** of the analyte is a desired result of a spectrochemical analysis and almost never obtained directly as a result of an absolute measurement of an optical signal. It is obtained indirectly through calibration, subtraction of blanks, comparison with standards and other procedures.

– **Total spectrochemical signal** is defined as the unmodified readout signal obtained from the measurement of a sample or standard

– **The blank/reference signal** is the readout signal of the blank. It includes the background signal due to optical signals from the sample container and the concomitants in the blank.

– **The analytical signal** is obtained by subtracting blank emission signal from the total spectrochemical signal

## 1.3 Expression of Analytical Information

- The analytical signal is related to the analyte concentration and other variables by **Calibration function,  $f$** , defined by  $S = f(C_a, \lambda, x_i)$   $S = \text{signal}$   $C = \text{conc.}$   $x_i = \text{temp, time... etc.}$
- The dependence of calibration function on a specific variable is often given a particular name. E.g. A plot of the analytical signal versus analyte concentration, with all the other variables held constant, is called the **calibration curve, the working curve or the analytical curve**.
- The **analytical function,  $g$** , is the inverse of the calibration function  $C_a = g(S)$   
if  $S = 10^{-4} C_a$   $C_a = 10^4 S$  and it provides a direct method for calculating the analyte concentration from the measured analytical signal for a given set of experimental conditions.
- The instrumental and chemical parameters need to be optimized to get maximum analyte signal.
- **Signal to background ratio, S/B;**  $S = \text{analytical signal}$
- **Relative Standard Deviation (RSD);**  $B = \text{sum of background spectral signals from other species or the sample container}$
- **Signal to Noise Ratio (S/N);**  $N = \text{root-mean square noise in the analytical signal}$

$$\text{RMS noise} = \sqrt{\frac{\sum_{i=1}^n (X_i - \frac{\sum_{i=1}^n X_i}{n})^2}{n}}$$

$$\%RSD = \frac{s}{\bar{x}} \times 100$$

$$\text{SNR} = \frac{\text{signal}}{\text{RMS noise}}$$

$$S/N = (\text{RSD})^{-1}$$

$$s_N = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \bar{x})^2}$$

$s$ , is equal to the [standard deviation](#),  $\bar{x}$  is equal to the [mean](#)



# 1-4 Evaluation Criteria in Spectrochemical Techniques

- Practical Considerations:
  - Cost
  - Sample size
  - Simplicity
  - Portability
  - Robustness
  - Speed
  - Sample preparation
  - Automation
  - Interferents
  
  - Selective technique or specific technique: freedom from interference

## Figures of Merit:

Accuracy: How close the measured analyte conc. is to the true analyte conc. in the sample

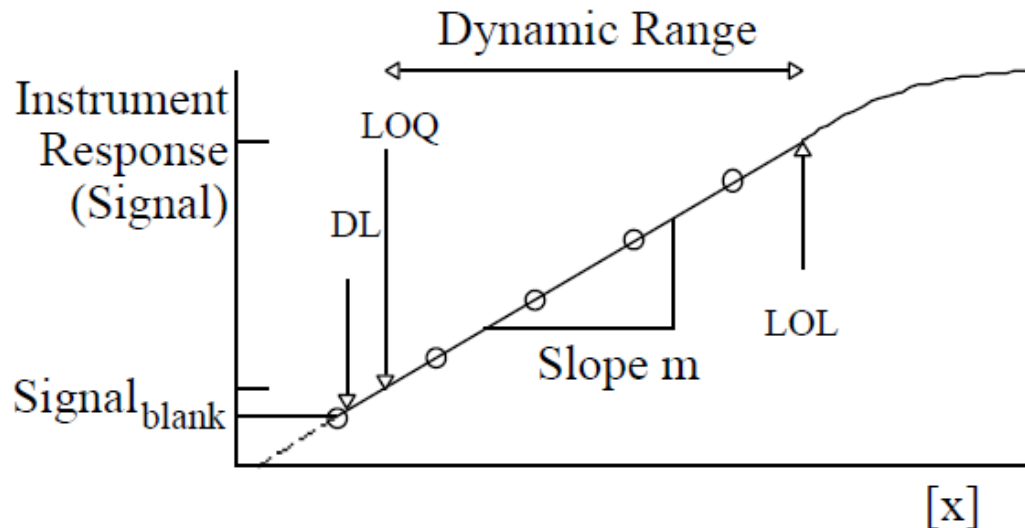
Precision: % RSD, reproducibility of repetitive measurements of equivalent analyte solutions. Averaging may be used to improve precision.

Sensitivity: usually indicates the response of the instrument to changes in analyte conc.

- and is expressed as the slope of the calibration curve or
- the change in analytical signal per unit change in analyte concentration.

Sometimes, refers to the ability to distinguish concentration differences and thus takes into account the precision of measurements

## Figures of Merit



**Detection limit:** the analyte concentration yielding an analytical signal equal to 2 or 3 times the standard deviation of a blank measurement

**Limit of quantification; LOQ:** 10 times the standard deviation of a blank measurement

**Limit of Linearity; LOL:** the concentration at which the calibration curve departs from the linearity.

**Dynamic Range:** the range between LOQ and LOL. To be useful an analytical method should have a dynamic range of at least 2 orders of magnitude.